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Fabrication and Relaxation Dynamics of Holographically Induced Surface Relief Gratings on Azo-substituted Polymer Film

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Recently, the holographic recording of a surface relief grating (SRG) on the azobenzene-substituted photochromic polymer film upon irradiation of two interfering beams of a low power laser was discovered [1, 2] and many studies have been carried out from the view point of fundamental interest and for the practical applications [3, 4]. Due to the cyclic *trans-cis-trans* photoisomerization of azobenzene in the side chain, mass-transport was induced and SRG was formed corresponding to the distribution of intensity of interfered light. Several models to explain the formation mechanism of SRG were proposed such as radiation force caused by a light intensity gradient[5], interaction between dipoles of azobenzene moieties (mean-field theory)[6], fluid mechanics model based on Navier-Stokes equation[7, 8]. However, the detailed formation mechanism of SRG has not been clarified yet. In this study, the relaxation dynamics of azo-polymer after stopping the writing laser beams was investigated under various conditions, and the SRG formation mechanism is also discussed.

Figure 1 shows the molecular structure of the polyacrylate containing azobenzene moiety in the side chain (azo-polymer). This polymer was dissolved in chloroform and spin-coated on a glass substrate and then heated up in order to remove the solvent completely. The thickness of the film was about 1 μm. Then SRG was formed using an interferential light irradiation system shown in the inset of Fig.2. The recording light source was Ar^+ laser (Beamlok2060-4S : Spectra Physics) with a wavelength of 488nm. The two recording lights were circularly polarized, and the angle between two recording laser beams was 40 degrees throughout this study. In order to monitor the formation of SRG, the intensity of a transmitted and diffracted beam of a He-Ne laser light (632.8nm) was measured by a photodiode and diffraction efficiency was evaluated. Color filter O-56 (TOSHIBA) which cut off the light whose wavelength was shorter than 560nm was placed in front of the

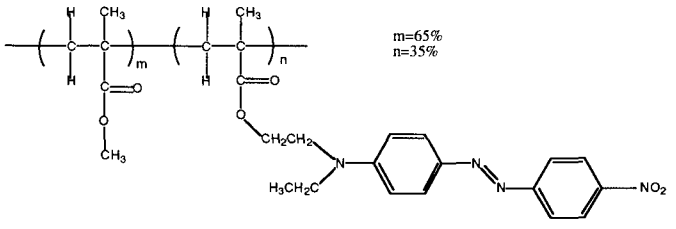

Fig.1. Molecular structure of Azo-polymer used in this study

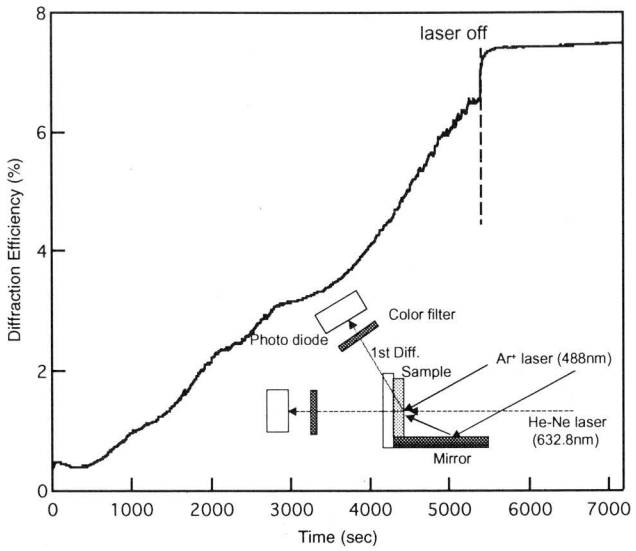

Fig.2. Irradiation time dependence of diffraction efficiency
(inset: interferential light irradiation system).

detector not to detect the writing Ar^+ laser light. Figure 2 shows irradiation time dependence of diffraction efficiency of He-Ne laser from the formed SRG. The holographic recording was conducted for 90 minutes, and after stopping irradiation of Ar^+ laser light, diffraction efficiency was also monitored to evaluate relaxation dynamics under dark condition. The recorded SRG profile was observed using an atomic force microscope (AFM), (JSTM-4200A : JOEL). Figure 3 shows the AFM profile of formed SRG on the azo-polymer film. From this figure, it was confirmed that the SRG with about 100nm height and 700nm periodicity was recorded.

As shown in Fig.2, the increase of diffraction efficiency even after stopping recording laser light irradiation is observed. This means that some relaxation process occurs without laser light irradiation. In the discussion on the relaxation process, diffraction both from surface relief grating and from refractive index

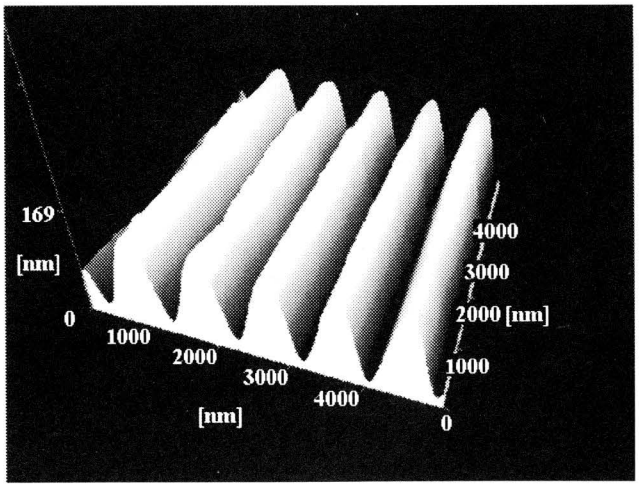

Fig.3. AFM profile of the formed surface relief grating on the azo-polymer film.

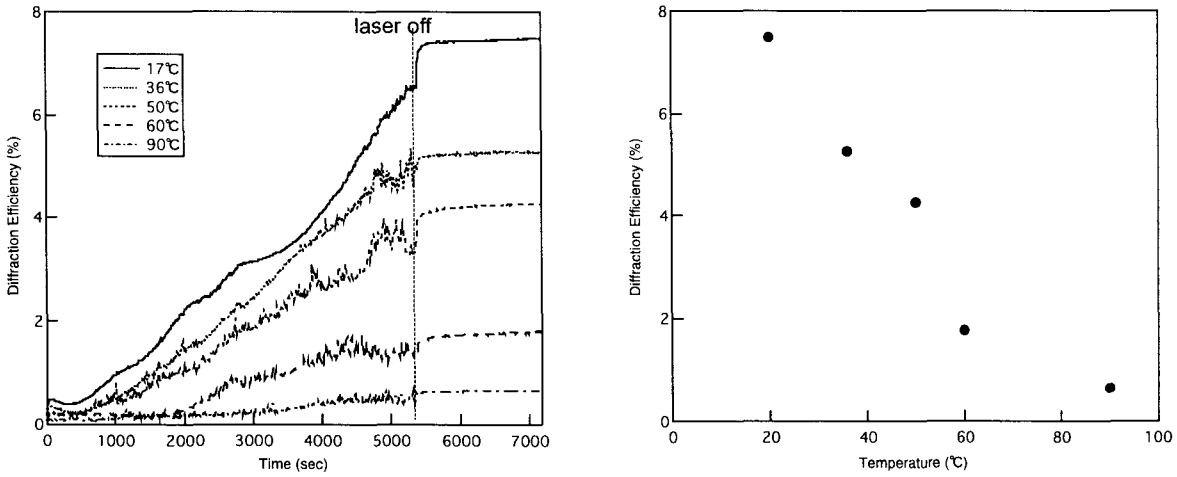

Fig. 4 (a) the irradiation time dependence of diffraction efficiency at various temperatures (b) temperature dependence of formation of SRG

grating should be considered. Based on these considerations, possible models for explaining the growth of diffraction efficiency after stopping laser light irradiation can be summarized as follows. (1) Changing of relief profile (relief height) itself. This may be attributed to the relaxation of polymer main chain. (2) *Cis-trans* thermal isomerization of azobenzene. (3) Orientational change of azo chromophore in the side chain. This should cause the change in birefringence and absorption. If these diffraction efficiency growth phenomena originate from *cis-trans* thermal isomerization of azobenzene, it should be more effective and the diffraction efficiency grows faster in higher temperature, because *cis* form of azobenzene is unstable thermally, and *cis-trans* thermal isomerization occurs more effectively in higher temperature. To examine whether this thermal isomerization effect plays a crucial roll or not, the recording of SRG was performed at various temperatures.

Figure 4 (a) shows the irradiation time dependence of diffraction efficiency at various temperatures, and Fig.4 (b) shows temperature dependence of final values of diffraction efficiency (corresponds to that of 7200 sec in Fig.4 (a)). These figures clearly show that the formation of SRG can be conducted more efficiently in lower temperatures. In other words, *trans-cis-trans* isomerization didn't occur effectively to form SRG at higher temperature.

Figure 5 shows the normalized growth of diffraction efficiency after stopping of laser irradiation. The diffraction efficiency increases faster at lower temperatures. From this result, the growth of diffraction efficiency can be considered not from *cis-trans* thermal isomerization of azobenzene but from relaxation process of polymer main chain and/or azobenzene in the side chain. Although the driving force in the relaxation process is not clarified now, the temperature dependence of polymer elasticity and viscosity can be considered to affect to the driving force of the diffraction efficiency growth and migration of polymer

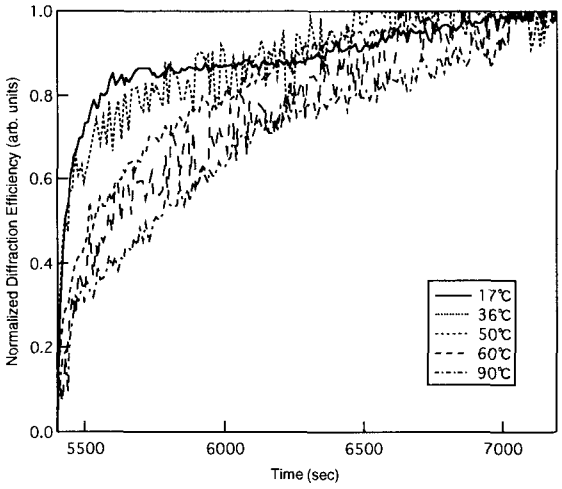

Fig. 5 (a) normalized growth of diffraction efficiency after stopping laser light irradiation at various temperatures.

main chain.

In conclusion, concerning the holographic formation of SRG on azo-polymer film, the relaxation process after stopping laser light irradiation was investigated at various temperatures. It was found that the growth of diffraction efficiency after stopping laser light irradiation didn't originate from *cis-trans* thermal isomerization. For a complete understanding of these relaxation phenomena, both SRG profile change (relaxation of polymer main chain) and orientation change of azo-chromophore in the side chain should be considered. To evaluate the effect of these relaxation to the growth of diffraction efficiency after stopping laser light irradiation, polarization effect of a probe He-Ne laser light is studied now. From the understanding of these relaxation processes, the information about the formation mechanism of SRG may be obtained.

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